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A comparison of very short lived halocarbon (VSLs) and DMS aircraft measurements in the tropical west Pacific from CAST, ATTREX and CONTRAST

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Abstract. We present a comparison of aircraft measurements of halogenated very short lived substances (VSLs) and dimethyl sulphide (DMS, C₂H₆S) from a co-ordinated campaign in January–February 2014 in the tropical west Pacific. Measurements were made on the NASA Global Hawk, NCAR Gulfstream-V High-performance Instrumented Airborne Platform for Environmental Research (GV HIAPER) and UK Facility for Airborne Atmospheric Measurements (FAAM) BAe-146 (see Sect. 2.2) using four separate gas chromatography–mass spectrometry (GC-MS) instruments: one operated by the University of Miami (UoM), one from the National Center for Atmospheric Research (NCAR) and two from the University of York (UoY). DMS was measured on the BAe-146 and GV. The instruments were inter-calibrated for halocarbons during the campaign period using two gas standards on separate scales: a National Oceanic and Atmospheric Administration (NOAA) SX-3581 standard representative of clean low-hydrocarbon air, and an Essex canister prepared by UoM, representative of coastal air, which was higher in VSLs and hydrocarbon content. UoY and NCAR use the NOAA scale/standard for VSLs calibration, and UoM uses a scale based on dilutions of primary standards calibrated by GC with FID (flame ionisation detector) and AED (atomic emission detector). Analysis of the NOAA SX-3581 standard resulted in good agreement for CH₂Cl₂, CHCl₃, CHBr₃, CH₂Br₂, CH₂BrCl, CHBrCl₂,

CHBr₂Cl, CH₃I, CH₂ICl and CH₂I₂ (average relative standard deviation (RSD) < 10 %). Agreement was in general slightly poorer for the UoM Essex canister with an RSD of < 13 %. Analyses of CHBrCl₂ and CHBr₃ in this standard however showed significant variability, most likely due to co-eluting contaminant peaks, and a high concentration of CHBr₃, respectively. These issues highlight the importance of calibration at atmospherically relevant concentrations (~0.5–5 ppt for VSLs; see Fig. 5 for individual ranges). The UoY in situ GC-MS measurements on board the BAe-146 compare favourably with ambient data from NCAR and UoM; however the UoY whole-air samples showed a negative bias for some lower-volatility compounds. This systematic bias could be attributed to sample line losses. Considering their large spatial variability, DMS and CH₃I displayed good cross-platform agreement without any sampling bias, likely due to their higher volatility. After a correction was performed based upon the UoY in situ vs. whole-air data, all four instrument datasets show good agreement across a range of VSLs, with combined mean absolute percentage errors (MAPEs) of the four platforms throughout the vertical profiles ranging between 2.2 (CH₂Br₂) and 15 (CH₃I) % across a large geographic area of the tropical west Pacific. This study shows that the international VSLs calibration scales and instrumental techniques discussed here are in generally good agreement (within ~10 % across a range of VSLs), but that

losses in aircraft sampling lines can add a major source of uncertainty. Overall, the measurement uncertainty of bromocarbons during these campaigns is much less than the uncertainty in the quantity of VSLs bromine estimated to reach the stratosphere of between 2 and 8 pptv.

1 Introduction

Halogenated very short lived substances (VSLs) are defined as having atmospheric lifetimes shorter than tropospheric transport timescales, i.e. of around 6 months. VSLs (and their degradation products) are an important source of reactive halogens to the lower stratosphere (Carpenter et al., 2014; Hossaini et al., 2015). The major source of brominated (e.g. CHBr_3 and CH_2Br_2) and iodinated (e.g. CH_3I) VSLs is the ocean, due to production by phytoplankton (Tokarczyk and Moore, 1994; Quack and Wallace, 2003); macro algae (Carpenter and Liss, 2000; Carpenter et al., 2000; Chance et al., 2009; Goodwin et al., 1997; Leedham et al., 2013; Schall et al., 1994; Sturges et al., 1993); bacteria and detritus (Asare et al., 2012; Hughes et al., 2008); and, for CH_3I , photochemically (Happell and Wallace, 1996; Richter and Wallace, 2004). However, major uncertainties exist regarding the relative contribution of individual sources (Carpenter and Liss, 2000). Global distributions and controls of VSL emissions are also not well known, exacerbated by large spatial variability in sea–air fluxes (Carpenter et al., 2005; Archer et al., 2007; Ziska et al., 2013; Stemmler et al., 2013; Orlikowska and Schulz-Bull, 2009). These are important considerations as deep convection in the tropics can rapidly transport VSLs to the upper troposphere–lower stratosphere (UTLS) and make a significant contribution to photochemical ozone depletion (Von Glasow et al., 2004; Salawitch et al., 2005; Yang et al., 2005; Montzka et al., 2011; Saiz-Lopez et al., 2012; Feng et al., 2007; Laube et al., 2008; Sinnhuber and Meul, 2015). Due to deep convection, the tropical west Pacific supplies the largest source of stratospheric air (Fueglistaler et al., 2004; Bergman et al., 2012). VSLs are currently estimated to contribute 2–8 ppt of bromine to the stratosphere (Carpenter et al., 2014). Dimethyl sulfide (DMS) is also produced biogenically in the ocean and is the largest source of organic sulfur to the marine boundary layer (Cline and Bates, 1983; Nguyen et al., 1983; Andreae, 1986; Ferek et al., 1986). It affects the Earth's radiation budget and climate as an important aerosol and cloud condensation nuclei precursor.

Numerous global atmospheric transport models now include the VSLs CHBr_3 and CH_2Br_2 (Hossaini et al., 2016), driven by one of three ocean emission inventories by Liang et al. (2010), Ordóñez et al. (2012) or Ziska et al. (2013). Based on few measurements from limited geographical areas, these inventories are poorly constrained (Ashfold et al.,

2014) and contribute significantly to model uncertainties (Hossaini et al., 2013).

The Liang et al. (2010) and Ordóñez et al. (2012) top-down inventories use simple latitudinal bands to define emissions, with equatorial and coastal enhancements informed by measurements. Major effort has been made to combine ocean and atmospheric VSL datasets and provide a bottom-up (seawater-based) emission inventory (Ziska et al., 2013). For CHBr_3 , the Ziska inventory results in the lowest mean absolute percentage error (MAPE) between the forecast and the measurements, compared to the other inventories (Hossaini et al., 2016). However for CH_2Br_2 , the Ziska et al. (2013) inventory tends to produce model overestimation of atmospheric mixing ratios, while Liang et al. (2010), with the lowest emission flux, performs favourably (Hossaini et al., 2016). One reason for poorer performance of the Ziska et al. (2013) inventory for CH_2Br_2 could be errors associated with measurements and variability between the compiled datasets, likely due to the lack of a common VSL calibration scale.

Hossaini et al. (2016) observed that, within the 12 models they compared for the Atmospheric Tracer Transport Model Intercomparison Project (TransCom-VSLs), no single emission inventory was able to provide the best agreement between model and measurement at all surface observation comparison locations.

In order for emissions inventories based upon collated measurement datasets to provide an accurate representation of surface VSL distribution, it is imperative that datasets be properly inter-calibrated and compared such that their errors and variability are well characterised.

2 Experimental

2.1 Overview of campaigns

The dataset inter-comparison consisted of three aircraft-based campaigns: Co-ordinated Airborne Studies in the Tropics (CAST; Harris et al., 2016), CONvective Transport of Active Species in the Tropics (CONTRAST; Pan et al., 2016) and Airborne Tropical Tropopause Experiment (AT-TREX). All three campaigns were carried out in the tropical west Pacific in January–February 2014 and centred around the island of Guam (13.5° N, 144.8° E). No side-by-side comparison flights were carried out, so we compare measurements on a statistical basis across a large geographic area of the west tropical Pacific where all four instruments sampled (130–165° E, 0–15° N, Fig. 1, dashed purple boxes). The comparison region was limited to an altitude of 8 km, the ceiling for the BAe-146 data. A total of 1725 data points (158 AWAS, 490 TOGA, 629 WAS and 458 in situ GCMS) were sampled within this comparison region.

The comparison region contained predominantly open-ocean, well-mixed air masses, with some coastal input. Elevated surface levels of VSLs, including CHBr_3 , were ob-

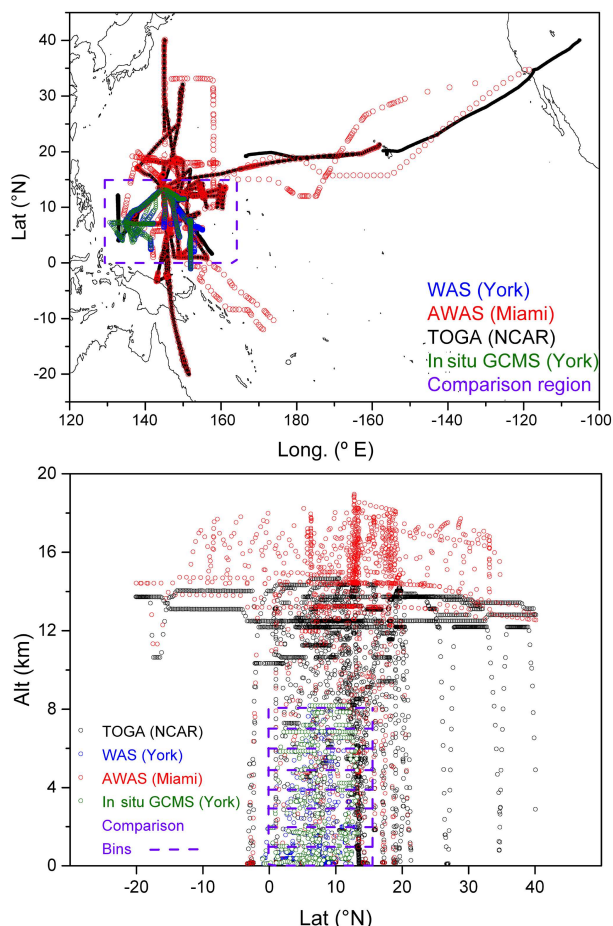


Figure 1. Top: spatial distribution of all CAST, CONTRAST and ATTREX VLS measurements, coloured according to instrument: WAS (blue), AWAS (red), TOGA (black) and in situ GCMS (green). Box (purple dashes) depicts region chosen for sample inter-comparison. Bottom: vertical distribution of all CAST, CONTRAST and ATTREX VLS measurements, coloured according to instrument as per Fig. 1. Purple dashed boxes show individual comparison bins (see Sect. 3.2).

served near to coastal areas and islands; this is discussed on a case-by-case basis. Due to the relative homogeneity of open-ocean VLS emissions (e.g. Ziska et al., 2013), as shown by the relatively low variability of altitude-averaged data (see Sect. 3.2), outside of the coastal areas we consider that a statistical comparison of data provides a good analysis of measurement comparability.

2.2 Methods

The comparison involved four different instruments using individual calibration gas standards and analysing air samples from three separate measurement platforms. These platforms were the UK Facility for Airborne Atmospheric Measurements (FAAM) BAe-146 large research aircraft (CAST

campaign), the National Science Foundation /National Center for Atmospheric Research (NSF/NCAR) Gulfstream-V High-performance Instrumented Airborne Platform for Environmental Research (GV HIAPER, CONTRAST campaign) and the National Aeronautics and Space Administration (NASA) Northrop Grumman Global Hawk (GH, ATTREX campaign). On board the FAAM BAe-146, air samples were analysed by the UoY both by an in situ gas chromatograph–mass spectrometer (in situ GC-MS, coloured green in figures) and offline as whole-air samples (whole-air sampler (WAS), coloured blue in figures) by a separate GC-MS. Air samples captured by the NSF/NCAR GV and the NASA Global Hawk were analysed by the UoM and hereto referred to by the collection apparatus name: Advanced Whole Air Sampler (AWAS, coloured red in figures). The fourth instrument was the NCAR in situ GC-MS on board the GV, referred to as the Trace Organic Gas Analyzer (TOGA, coloured black in figures). See Table 1 for a summary.

2.2.1 Whole-air sampler (WAS)

Samples were collected as described in Andrews et al. (2013) using evacuated 3 L SilcoCan canisters (Restek) sealed by pneumatically operated bellows valves (Swagelok, P/N SS-BNVVCR4-C). Air was drawn in through a forward-facing air sampling pipe on the exterior of the aircraft and pressurised into the canisters using a metal bellows pump (Senior Aerospace PWSC 28823-7) to approximately 275 kPag (40 psig). The FAAM BAe-146 has a much lower operating ceiling than the other aircraft but can profile down to ~ 15 m above sea level (a.s.l.) and sampled frequently in the marine boundary layer. Due to operating at tropical latitudes, this resulted in much higher than usually experienced humidity in the sample lines, pump and canisters. Analysis of the cylinders was carried out in the aircraft hangar, usually within 72 h of collection. The stability of the measured VLSs in the WAS canisters was quantified over the course of 1 month, and drift was found to be < -0.01 ppt per 24 h for all species (Andrews et al., 2013). The positive pressure in the canisters was utilised for sample introduction into the instrument to avoid contamination from any potential leaks associated with reduced pressure sampling using a pump. Sample humidity was controlled using a -30°C glass cold trap to remove water without loss of the analytes (Andrews et al., 2015; Swan et al., 2015). Two litres of sample was pre-concentrated onto the cooled (-30°C) adsorbent trap (Tenax TA) of a thermal desorption unit (TDU, Markes UNITY 2-CIA-T) and desorbed with a 2 mL min^{-1} helium carrier at 250°C onto a capillary column (Restek RTX502.2, 30 m, 0.25 mm I.D., $1.4\text{ }\mu\text{m}$ film thickness) of a gas chromatograph (Agilent 7890A) held at 40°C for 3 min and then ramped at $25^{\circ}\text{C min}^{-1}$ to 250°C and held for 3 min. Analytes were detected using a mass selective detector (MSD, Agilent 5977 Xtr source) with 19 selected ion windows monitoring a total of 46 ions, a qualifier and quantifier per analyte. The MSD

Table 1. Summary of measurement platforms, instruments and institutions. Colour code refers to the colour of data displayed in figures.

Measurement	Platform	Instrument/institution	Colour code
In situ GCMS	NCAS/FAAM BAe-146	University of York, in situ GCMS	Green
WAS	NCAS/FAAM BAe-146	University of York, ground-based GCMS	Blue (orange un adjusted)
AWAS	NCAR GV, NASA GH	University of Miami, ground-based GCMS	Red
TOGA	NCAR GV	NCAR TOGA, in situ	Black

source and quadrupole temperatures were 250 and 200 °C, respectively. Calibration of the WAS instrument was carried out daily for VLSs using a NOAA calibration gas standard in a electropolished stainless-steel canister (SX-3581 Essex Cryogenics) filled in October 2013 and quantified using the NOAA 2003 scale for CH₂Cl₂, CHCl₃ and CHBr₃; NOAA 2004 scale for CH₃I and CH₂Br₂; and a provisional scale for CH₂BrCl, CHBrCl₂, CHBr₂Cl, CH₂ClI and CH₂I₂ – the latter based on a limited number of standards in which mole fractions have remained consistent since 2009. NOAA SX-3581 contains an ambient air matrix with halocarbon concentrations enhanced to a few parts per trillion (Hall et al., 2014). For DMS, a custom standard was prepared at the University of York containing an atmospherically relevant concentration of DMS (~17 ppt) diluted with nitrogen (BOC N6 grade). This was calibrated against a KRISS primary DMS standard. Halocarbon concentrations in Essex cylinders were monitored at UoY and were found to be stable for > 4 years after production, even for species such as CH₂I₂, which is often unstable in cylinders (Andrews, 2013). UoY have purchased three NOAA calibration cylinders: SX-3570, SX-3576 and SX-3581, which all compared well to one another's quoted values (< 4 %RSD) according to our analyses.

2.2.2 In situ gas chromatograph–mass spectrometer

VSLs measurements were made in-flight using a thermal desorption (TD) GC-MS system mounted in the BAe-146 cabin. Sample air was drawn from the same main sample line as for WAS and shared the same metal bellows pump within the cabin. Air was diverted from the WAS pumping system before the sample line entered the aircraft hold and dried using a multi-core counter-current Nafion drier (Perma Pure PD series). Samples were alternately pre-concentrated or analysed using dual, parallel adsorption traps (Tenax TA, Markes International TT-24/7), cooled to 0 °C. Analytes were refocused at the head of the column using liquid CO₂ prior to separation (10 m, 180 µm I.D., 1 µm film, Restek RTX502.2 column; 50 to 150 °C at 40 °C min⁻¹) by GC (Agilent 6850) and detection by electron impact MS selected ion monitoring (Agilent 5975C), calibrated pre-flight against the WAS gas standard (NOAA, SX-3581). Instrument temporal resolution, and associated sample integration period, was 5 min.

2.2.3 Advanced Whole Air Sampler

The AWAS on the GV aircraft used custom-built electropolished stainless-steel canister modules (1.3 L), with 12 canisters per module connected by a welded 1/4 in. (6.35 mm) stainless-steel manifold. Typically, five modules (60 canisters) were collected per research flight. The canisters were sealed with pneumatically operated bellows valves (Swagelok, P/N SS-BNVVCR4-C, Swagelok, USA), and sample control was by computer command, in either an automatic or on-demand mode. The canisters were pressurised by two metal bellows dual-stage pumps (Model 28823-11, Senior Aerospace, Sharon, MA, USA), with a parallel input in the first two stages followed by serial connections in the second pump to provide final pressures of approximately 345 kPaa (50 psia). Each module was cleaned with multiple, heated flushes of pure nitrogen, with a final addition of 25 torr of water vapour to passivate interior surfaces under dry (upper-tropospheric) conditions. The inlet was an unheated stainless-steel line connected to a HIAPER Modular Inlet (HIMIL; <http://www.eol.ucar.edu/homes/dcrogers/Instruments/Inlets/>) with the sample line at 90° relative to the airflow in the HIMIL. A heat exchanger was installed between the pump outlet and the sample inlet to remove bulk water from the sample flow. This inlet was the same as used on the HIPPO campaign for trace gas sampling. Sample flow through the system was dependent on altitude and ranged from about 30 to 5 mL min⁻¹. The GH 30 sampler consisted of modular sets of canisters of either 10, 8 or 6 cans per module. The 1.3 L canisters were custom-built by Entech, Inc. to include a specially bent inlet tube to accommodate the module design. Each canister is coated with a proprietary silica-based coating. The canisters were sealed with Parker Series 99 valves (P/N 099-0403-900, Parker Hannifin Corp., Hollis, NJ, USA). Sample pumps were identical to the GV arrangement, but no heat exchanger was installed on the GH. An unheated, forward-facing inlet with an exit for large particles and liquid water was installed on the underside of the GH aircraft. Sample canister preparation for the GH was the same as for the GV sampler.

Trace gas measurements from both aircraft were analysed on a single system. The system used a Markes canister interface (CIA) and a UNITY 2 system connected to an Agilent 5975 GC-MSD. The samples were dried in a –20 °C stainless-steel water trap, followed by a 50 mm sec-

tion of nafion tubing (MD-050-24-FS-2; Perma Pure, Toms River, NJ) to further dry the sample. The sample was pre-concentrated on a Markes ozone precursor trap (Markes UT1703P-2S) held at -37°C . Sample size was 800 cm^3 , with a controlled flow of 80 sccm . The sample was thermally desorbed at 300°C for 6 min. The sample was split in the GC oven, with approximately two-thirds (525 cm^3) directed to a $30\text{ m} \times 0.25\text{ mm} \times 5\text{ }\mu\text{m}$ Alumina PLOT column (HP-AL/S, Agilent Technologies) with a flame ionisation detector. A short (1 m) section of GasPro column was added to the column end to facilitate separation of HFC-143a from ethyne. The remaining flow was sent to a $20\text{ m} \times 0.2\text{ mm} \times 1.12\text{ }\mu\text{m}$ DB-624 column (128-1324, Agilent Technologies). At the column exit, approximately 30 % (83 cm^3) was split in an Agilent capillary splitter and directed to an electron capture detector. The remaining sample (about 192 cm^3) was sent to the MSD. The oven temperature programme was -20°C (3 min) to 200°C at $10^{\circ}\text{C min}^{-1}$ (hold 4 min).

Calibration of the samples was done between every five samples. The calibration gas was a whole-air sample collected cryogenically at the Rosenstiel School of Marine and Atmospheric Sciences directly into an Essex 30 L cylinder. The calibration of the working standard was done by a series of dynamic dilutions of high concentration standards (SCOTT specialty gas) that had been previously measured by GC-AED and GC-FID using NIST standards to verify carbon and halogen responses. The method has been described in Schauffler et al. (1999).

2.2.4 Trace Organic Gas Analyzer

VSLs and DMS measurements were made in-flight using a three-stage pre-concentrator coupled to a GC-MS system mounted in the GV cabin. Sample air was drawn through a heated electropolished stainless-steel line by a metal bellows pump. The sampled air was not drawn through the pump, but a subsample from the main inlet line was drawn at 25 mL min^{-1} through a water trap (-25°C) and into the enrichment trap (-130°C) with a sample collection time of 35 s. Following this, the enrichment trap was heated at $25^{\circ}\text{C s}^{-1}$ from -130 to 100°C , and the pre-concentrated sample was transferred with helium carrier gas at 1 mL min^{-1} to the cryofocus trap which was cooled to -130°C . The cryofocusing trap was then heated, also at $25^{\circ}\text{C s}^{-1}$, from the cold set point to $+100^{\circ}\text{C}$, in the presence of 1 mL flow of He carrier gas, thereby injecting the sample onto the custom-designed GC. The GC was fitted with a Restek MXT-624 column (ID = 0.18 mm ; length = 8 m). The initial GC oven temperature of 25°C was held for 10 s followed by heating to 120°C at a rate of $110^{\circ}\text{C min}^{-1}$. The oven was then immediately cooled to prepare for the next sample. Sample processing time was 2 min. More details can be found in Apel et al. (2003). The system was calibrated with NOAA standards SX-3515 and SX 3562 prior to deployment.

2.2.5 MAPE calculation

In order to compare platforms, the MAPE (%) was calculated for each instrument at each altitude bin. This shows how much each instrument has differed from the mean concentration of all data. For example, for the WAS 0–1000 m bin,

$$\text{WAS MAPE}_{0-1000} = \frac{100\%}{n} \sum_{dp=1}^n \left| \frac{C_{\text{mean}} - \text{CWAS}_{dp}}{C_{\text{mean}}} \right|, \quad (1)$$

where n is the number of individual data points in the 1000 m altitude bin, dp is the individual instrument data point within the bin, C_{mean} is the mean concentration of all instrument data within the bin and CWAS_{dp} is the WAS individual data point concentration within the bin.

3 Results

3.1 Inter-calibration

The two instruments analysing the WAS and AWAS canisters, plus the in situ TOGA instrument, were briefly compared via inter-calibration during the campaign. The in situ GCMS calibration was directly linked to WAS and, due to operating constraints, did not take part in the comparison. A 5 L SilcoCan canister (Restek), identical except for volume to those used for sampling aboard the FAAM BAe-146, was evacuated and pressurised to 275 kPag (40 psig) from the NOAA SX-3581 cylinder used to calibrate WAS. The same canister was used routinely to transfer calibration gas to the in situ GCMS and for calibration during flights spanning multiple days. This was analysed by AWAS and TOGA within 72 h of filling, in the same manner as a WAS sample. The analysis was performed “blind” such that the concentrations were unknown to the analysts before providing their quantifications. A second inter-calibration gas provided by UoM was analysed by each institution. This was an Essex Cryogenics cylinder identical to NOAA SX-3581, filled cryogenically and analysed directly without decanting into a WAS canister. This sample was collected on the second-floor balcony of one of the campus buildings. Because the sample included traffic emissions as well as coastal marine emissions, the UoM cylinder contained a more complex background matrix and significantly higher CHBr_3 concentration than SX-3581.

Considering the simplicity of the inter-calibration exercise, with just a few analyses from each of the two cylinders, the values reported by each institution are closely comparable (Fig. 2). The average %RSD between institutions for all analytes was $< 10\%$ for the NOAA standard SX-3581. The average RSD for the UoM cylinder was slightly higher at $< 13\%$, mainly due to discrepancies in CHBr_3 and CHBrCl_2 . The discrepancy in CHBr_3 is likely due to the higher-than-ambient concentration in the UoM cylinder lying outside the

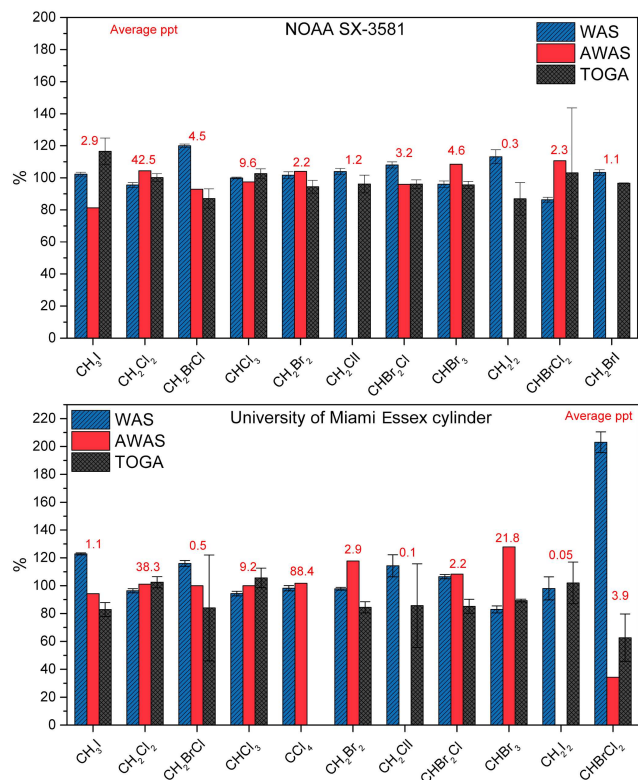


Figure 2. Inter-calibration results from the two calibration gases, shown normalised to the average for each species. Values in red denote concentrations of analytes in the respective standards; whiskers show \pm %RSD.

calibrated range of WAS and TOGA and highlights the importance of calibration at ambient concentration ranges. The error encountered in CHBrCl₂ can be attributed to contamination from co-eluting chromatographic peaks. The UoY monitored ions with m/z 127 and 129, which can suffer contamination issues but provide enhanced sensitivity when analysing “clean” air such as from open-ocean regions. It is likely that the TOGA instrument also suffers from contamination co-elution due to the fast chromatography employed. Air masses encountered during the CAST, CONTRAST and ATTREX campaigns were predominantly clean open ocean and more representative of the NOAA SX-3581.

3.2 Airborne data comparison

As the focus of the co-ordinated campaigns was to study the uplift of reactive halogens to the stratosphere, vertical profiles between platforms and instruments have been compared. This was performed by sorting the data into eight 1000 m altitude bins between sea level and 8 km pressure height, a range sampled by all three instruments. Note that the NASA Global Hawk did not sample at these altitudes, and therefore AWAS and TOGA are sampled from the same platform (GV). We first compare CHCl₃, a predominately

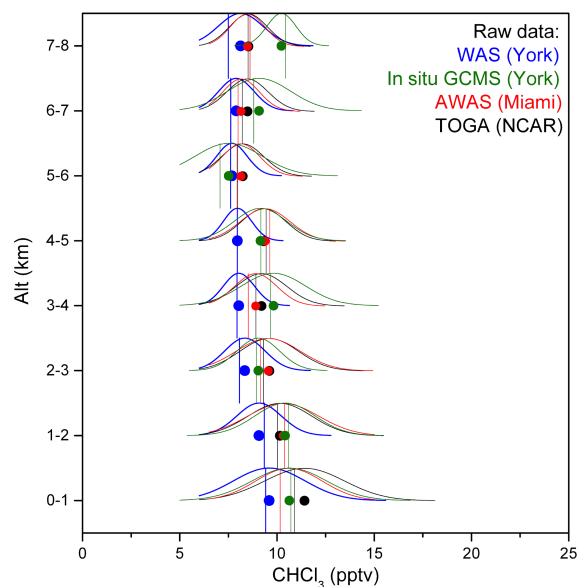


Figure 3. Comparison of unadjusted CHCl₃ mixing ratios measured by all four instruments, averaged into 1000 m altitude bins. Circles and vertical lines are the means and medians of the binned data with the distribution represented by a normal distribution curve.

biogenic gas emitted mainly from the ocean (Laturnus et al., 2002), with a moderately high background atmospheric mixing ratio (~ 10 ppt) and a relatively long atmospheric lifetime (150 days; Carpenter et al., 2014). All four raw (unadjusted) CHCl₃ datasets (Fig. 3) were comparable within bins to an average of 7 %RSD. To put this in perspective, the average %RSD of the CHCl₃ data points within each bin is 12 % for WAS, 16 % for in situ GC-MS, 15 % for AWAS and 25 % for TOGA.

This agreement between the datasets is very good considering that these measurements were taken on different times, on different days and at different locations; from multiple sampling platforms; and using different sampling techniques. However, the York WAS data are consistently lower than the in situ GCMS, AWAS and TOGA CHCl₃ data. This consistent offset is also apparent in other VSLs, such as CH₂Br₂ (Fig. 4, bottom left), which is present at much lower concentration than CHCl₃ and remains fairly constant throughout the entire profile.

Considering the profiles of all measured species, it is apparent that the UoY WAS CH₂Br₂, CHBr₃, CH₂BrCl, CHBrCl₂, CHBr₂Cl, CH₂Cl₂ and CHCl₃ data are consistently lower (19 ± 1 % throughout the vertical profile for CH₂Br₂) than the in situ GCMS, AWAS and TOGA measurements. We consider that the consistent bromo/chlorocarbon offset is not likely due to WAS sampling canister losses, which has been shown to be minimal (Andrews et al., 2013) and would likely have been seen during the inter-calibration when decanting SX-3581 into a WAS canister. One potential cause could be the sampling system aboard the FAAM

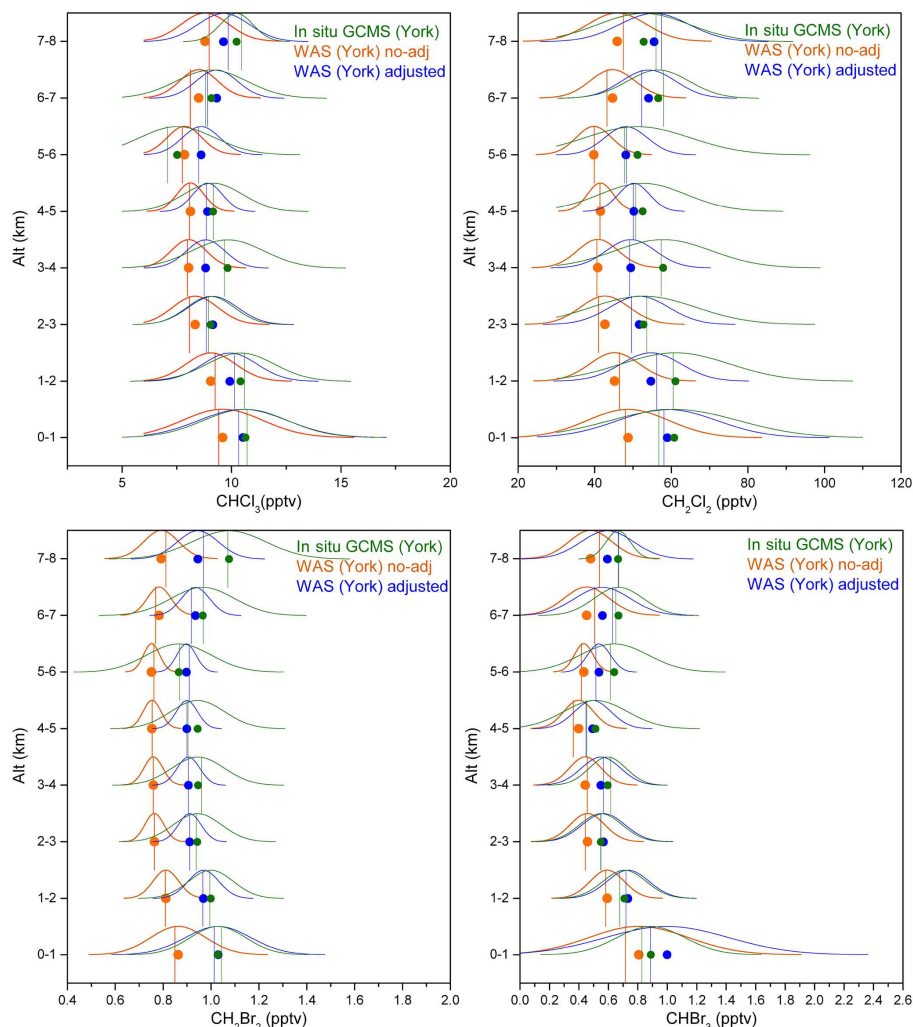


Figure 4. Vertical profile distribution bins showing a comparison of raw WAS data (orange), in situ data (green) and WAS data adjusted to in situ data via the method described in the text (blue).

BAe-146. The WAS system and in situ GCMS sample from the main science air intake, a “ram-air” type inlet that runs the length of the aircraft and exits the rear. Flow is diverted from this, through a metal bellows pump (Senior Aerospace PWSC 28823-7); the pressurised sample is supplied to the in situ GCMS and into the WAS cylinders (stored in the aircraft hold) via unheated, stainless-steel hoses; and it flows continuously whilst not sampling. Due to the high humidity and precipitation whilst operating in this region of strong convection, the WAS sampling lines often contained a large quantity of water that was removed pre-flight by pressure release from the WAS sample lines. The main inlet could not be flushed whilst stationary but was allowed to flush post-take-off before the sample pump was powered on.

In situ VLSL analysis on board the FAAM BAE-146 was performed by a GC-MS calibrated by the same method and sharing the same sample inlet and pump as for the WAS system, with the exception that the in situ GCMS sampled much

closer to the outlet of the pump, before the long lines to WAS canisters in the aircraft hold where water collected pre-flight. The in situ GC-MS did not have the precision of the WAS samples due to the fast chromatography employed, and profiles contained a larger data spread. However, the means and medians from the altitude binned data were consistently higher than for the WAS data and agreed well with AWAS and TOGA, supporting the theory that sampling line losses caused the offset in WAS VLSL concentrations (Fig. 4). We note that, unlike the bromo/chlorocarbons, CH_3I and DMS did not show a consistent offset between in situ and WAS data. This may have been due to their higher volatility and hence lower sampling losses compared to the rest of the substances analysed by UoY; these compounds also displayed a larger variability likely due to inhomogeneous ocean distributions, and therefore comparisons between datasets are not straightforward.

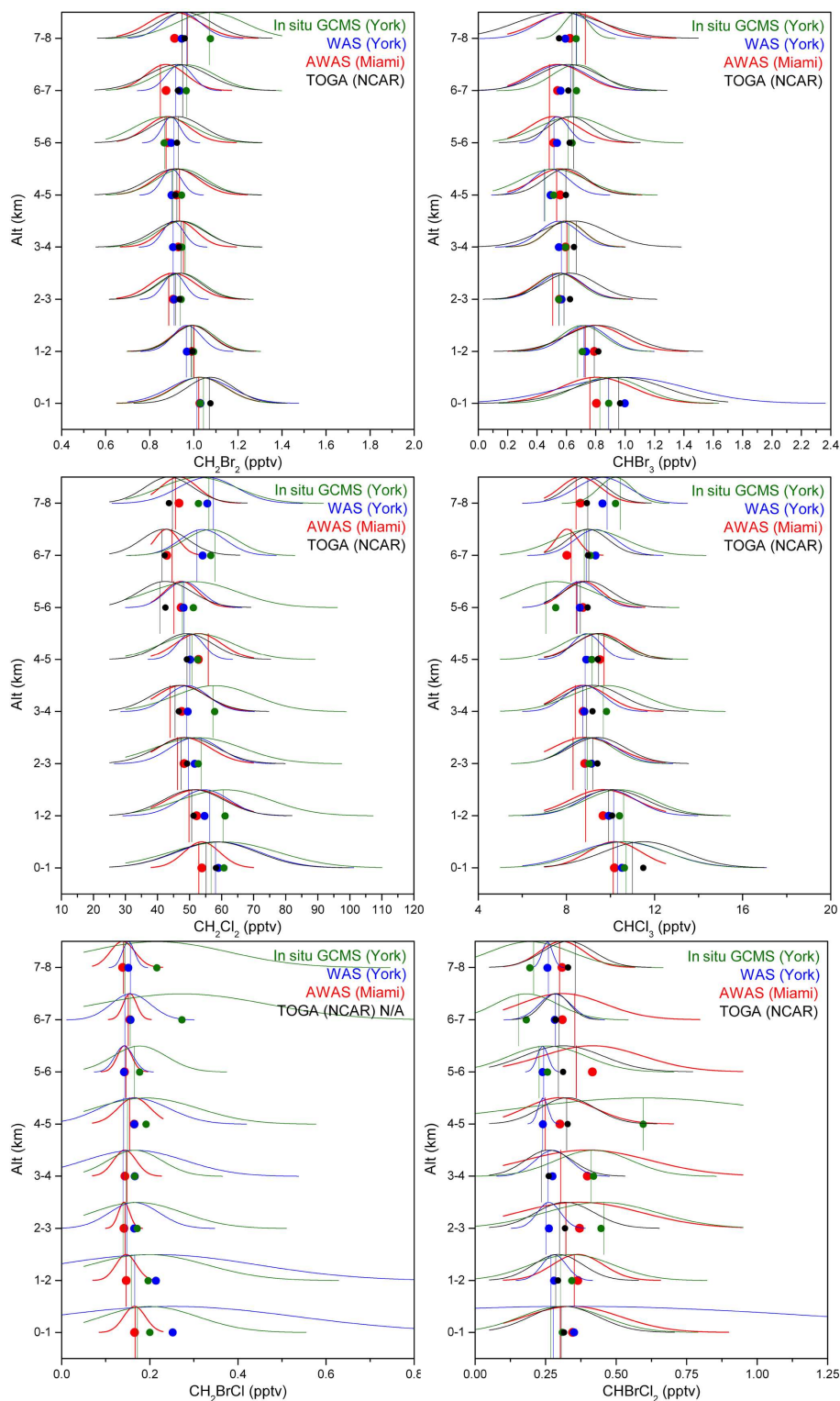


Figure 5.

The concurrent sampling of WAS and in situ GC-MS allowed a calculation of the WAS sampling offset for each affected compound. This was performed by averaging the off-

set at each altitude bin where the ratio of in situ GCMS : WAS was within 1σ of the average in situ GCMS : WAS ratio throughout the profile. This correction also improved agree-

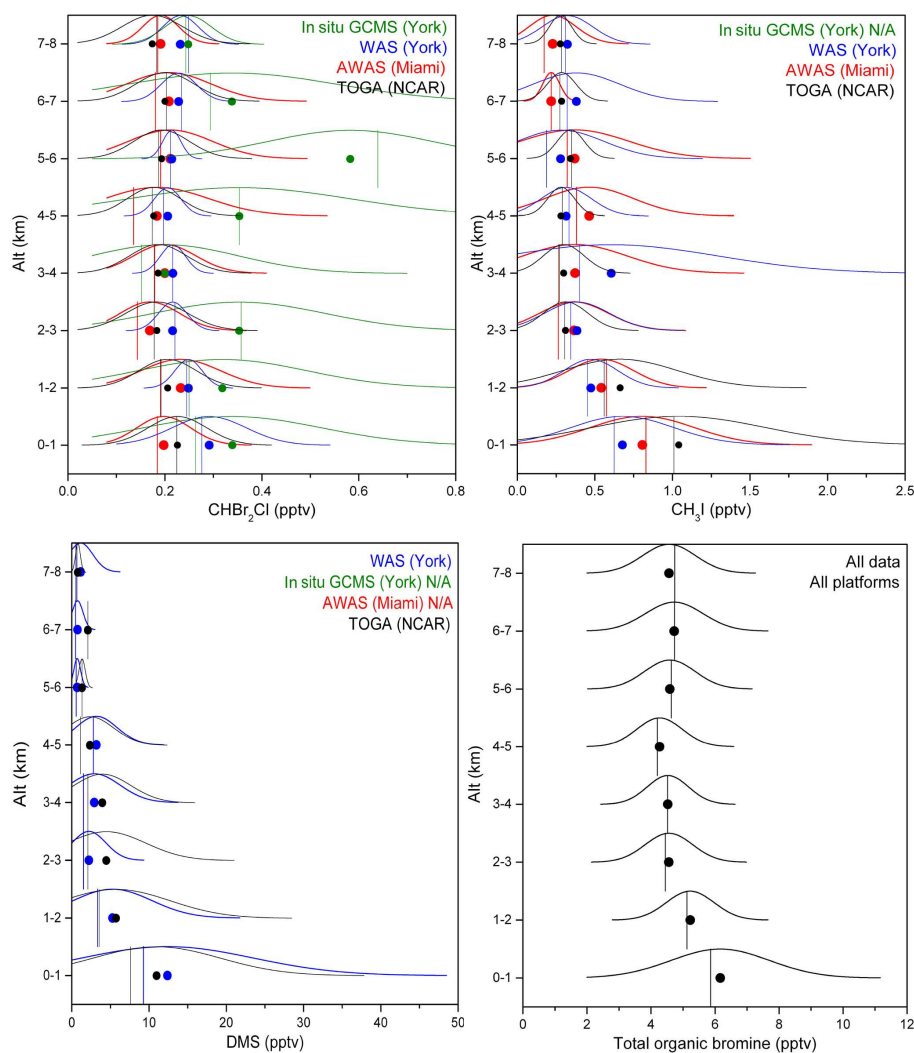


Figure 5. Vertical profile distribution bins for all species. WAS data have been adjusted as described in the text. “N/A” denotes cases where instruments have not analysed a compound. Bottom right: total organic bromine vertical profile calculated by the addition of all contributing bromine atoms from organic halocarbons, averaged across all instruments and sampling platforms.

ment of the UoY WAS data with AWAS and TOGA; for example CHCl_3 improved from agreement within 7 %RSD across profile averages to 5 %RSD, CHBr_3 from 19 % to 7 % and CH_2Br_2 from 11 to 3 %.

Above 5 km, the %RSD for many compounds increased with increasing altitude. This can be attributed to the fact that sampling of a range of relatively fresh to highly aged air masses occurred at these altitudes. The aged air masses, possibly entrained from higher altitudes or via long-range transport, can be identified by their characteristically high O_3 (Fig. 6) or low water concentrations, associated with lower VSLs concentrations. BAe-146 and GV transit flights were around 7 and 12 km, respectively. The probability of each aircraft intercepting such air masses increases as a function of time spent at those altitudes. Removing data where O_3 was greater than 50 ppb from each dataset removes this sam-

pling bias from the higher-altitude bins. All binned distribution plots here, with the exception of Fig. 3, have had the high- O_3 data removed, including for the calculation of WAS offset.

In the CHBr_3 data especially, samples below 1 km show enhanced concentrations from localised emissions such as the atoll of Chuuk (Fig. 7), Palau archipelago and Papua. WAS data showed the greatest enhancement as samples were taken from as low as 87 m a.s.l. and captured downwind plumes from the islands. In situ measurements such as the in situ GCMS and TOGA collect an integrated sample (2 min and 35 s, respectively) that represents an average across the distance the aircraft has travelled in that period of about 3–6 km, whilst fill times for grab samples such as WAS and AWAS are usually around 5–10 s (altitude-dependant). Therefore grab sampling can under/overestimate

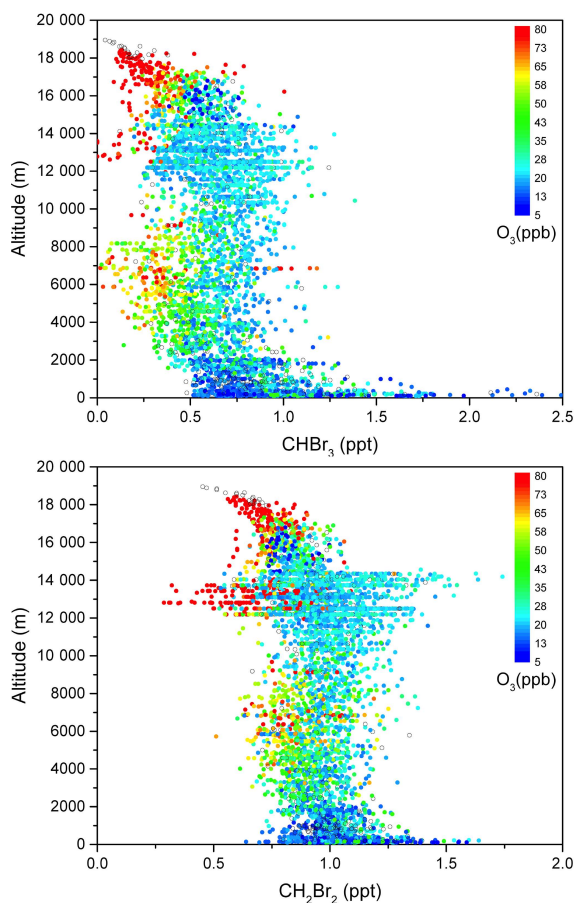


Figure 6. Vertical profiles of CHBr_3 (top) and CH_2Br_2 (bottom) combined datasets, coloured by ozone concentration. Empty circles depict measurements with no corresponding ozone measurement.

average concentrations, especially at low sampling frequency, whereas in situ measurements and high-altitude grab samples will intrinsically average air masses. This could account for the difference in CHBr_3 means between AWAS and TOGA and between WAS and in situ GCMS at altitudes less than 1 km.

Combined vertical profiles for CHBr_3 and CH_2Br_2 , the most atmospherically abundant bromocarbons (Fig. 6), show a distinct “C”-shaped profile with convective outflow visible at around 12–15 000 m. Low concentrations often coincided with enhanced O_3 concentration, consistent with air masses entrained from higher altitudes. In the case of the extremely low (< 0.5 ppt) CH_2Br_2 measured at ~ 13 000 m, the concentrations are lower than those measured at 18 000 m, where the ozone concentration is similar, and this may suggest sampling of different air masses from long-range transport. DMS was only quantified by WAS and TOGA and showed a highly spatially variable distribution below 2 km, characteristic of an oceanic source that is likely inhomogeneous, such as algal growth in areas of varying nutrient distribution. Despite such spatial variability, median averages compared well between

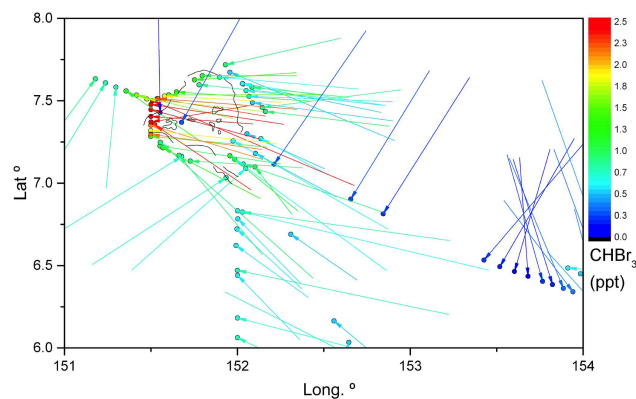


Figure 7. Localised island influence from Chuuk Atoll. Circles depict WAS sampling sites, and arrows show instantaneous wind direction and speed; both are coloured by CHBr_3 concentration.

the two platforms, which each sampled with large temporal and spatial differences. This suggests that wide-scale averaging across large water bodies could give consistent results for DMS.

3.3 Comparison of MAPE

MAPE was calculated as described in Sect. 2.2.5; a summary of the vertical profiles of the average MAPE across all platforms, averaged across altitude bins, is shown in Table 2. The average MAPE throughout the entire vertical profile for the four different instruments discussed here (in situ GCMS, WAS, AWAS, TOGA), compared to the mean observed concentrations, was 7.7 % for CHBr_3 and 2.2 % for CH_2Br_2 . Higher MAPEs were calculated for shorter-lived species, including CH_3I and DMS, where atmospheric variability is expected to make a large contribution to the spread of values measured across the different platforms.

In TransCom-VSLS, Hossaini et al. (2016) compared 12 models, using each models preferred emission inventory, with 7 recent aircraft campaigns including CAST. The model-to-measurement MAPE for all campaigns was ≤ 35 % for CHBr_3 and < 20 % for CH_2Br_2 . For most of the models studied by Hossaini et al. (2016), the model-to-ground-based observation MAPE over the latitudinal range $\pm 20^\circ$ was ~ 40 % for CHBr_3 and < 20 % for CH_2Br_2 . Therefore, the differences between measurement techniques within this study are much smaller than the current differences between models and measurements.

4 Conclusions

We present a combined dataset of VSLS aircraft profiles in the west tropical Pacific sampled by three different research groups on board the NCAR GV and FAAM BAe-146. Inter-calibration of standards showed that measurements agreed well (average RSD < 10 %) for the GC-MS

Table 2. Summary of calculated mean absolute percentage error (MAPE) between the four instruments (two instruments in the case of CH₂BrCl and DMS). Second column shows MAPE without the offset correction to WAS data applied. MAPE is shown for each altitude bin, and the average MAPE for the entire 0–8 km profile.

Species	MAPE (%)	MAPE (%) inc. WAS adjustment								
	0–8 km	0–1 km	1–2 km	2–3 km	3–4 km	4–5 km	5–6 km	6–7 km	7–8 km	0–8 km
CHBr ₃	9.9	10.5	9.7	7.3	4.0	8.6	7.0	6.8	7.6	7.7
CH ₂ Br ₂	5.1	3.1	2.4	1.6	1.0	2.3	2.8	1.6	2.5	2.2
CHCl ₃	3.7	4.4	2.3	1.6	3.4	3.6	2.0	5.2	3.4	3.2
CH ₂ Cl ₂	5.1	4.2	3.0	2.9	8.0	4.2	1.4	7.3	7.5	4.8
CH ₂ BrCl	10.0	2.5	0.2	7.4	11.7	12.1	12.6	12.0	9.4	8.5
CHBrCl ₂	19.2	6.9	14.2	16.4	19.8	11.8	22.2	8.4	8.5	13.6
CHBr ₂ Cl	11.0	3.2	13.1	7.4	9.6	12.8	14.1	11.4	10.9	10.3
CH ₃ I	15.0	15.6	22.3	7.1	18.5	19.4	17.0	13.2	6.6	15.0
DMS	29.5	21.4	4.7	30.0	21.4	20.1	49.3	23.3	65.6	29.5

analysis of CH₂Cl₂, CHCl₃, CHBr₃, CH₂Br₂, CH₂BrCl, CHBrCl₂, CHBr₂Cl, CH₃I, CH₂ICl and CH₂I₂ in a NOAA SX-3581 standard containing ambient VSLs levels. Inter-calibration using an in-house standard cylinder containing super-ambient VSLs levels and contaminant peaks showed less good agreement for some compounds.

Comparison of the UoY WAS and in situ GC-MS highlighted a negative bias in the WAS data which, by ruling out instrumental error and calibration scale differences via comparison and inter-calibration, we attribute to sampling losses in the BAe-146 WAS sampling lines during the campaign. A future re-design could minimise such losses by locating the WAS cylinder instrument rack close to a window blank connected with short lengths of heated, inert tubing, allowing more direct sampling, analogous to the GV TOGA inlet system.

Once the sampling losses are corrected for, agreement between averaged (by 1 km altitude bin) VSLs observations and the average of all (in situ GCMS, WAS, AWAS, TOGA) VSLs observations (MAPE) is very close, within 3 % for CH₂Br₂. Thus, it is apparent that spatial and temporal variability spanning months in this region of the west tropical Pacific is fairly low. The BAe-146 and GV never sampled the same air mass concurrently, and yet the average MAPE for CHBr₃, usually a more spatially variable species, throughout all profiles is ~7 %, a value similar to the average analytical uncertainty.

Our dataset is an encouraging result for global flux emission inventories as it suggests (1) relatively small analytical and scale errors across datasets and (2) low spatial and temporal variability in tropical open-ocean regions. Thus, it should be perfectly valid for data to be collated and potentially extrapolated over large spatial areas if systematic analytical biases can be eliminated. A step forward for the VSLs community would be to link their individual institutional calibration scales, both present data and historically, to one common scale, as in Hall et al. (2014). We have found

(Andrews, 2013) that the stability of even the most reactive halocarbons (CH₂ICl, CH₂I₂) is excellent in Essex Cryogenics air sampling canisters over long timescales (> 3 years) when prepared using the NOAA method (Hall et al., 2014).

5 Data availability

The dataset used is available at the NCAS British Atmospheric Data Centre (<http://catalogue.ceda.ac.uk/uuid/affe775e8d8890a4556aec5bc4e0b45c>, Smith, 2004).

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